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ACID-RESISTANT MATERIALS MADE FROM UZBEKISTAN MINERAL RAW MATERIAL

G. T. Adylov,[1] G. V. Voronov,[1] N. A. Kulagina,[1] E. P. Mansurova,[1] and M. Kh. Rumi[1]

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The possibility of using local raw material from Uzbekistan for production of acid-resistant materials was determined. The compositions of pastes made from porcelain stone from the Boinaksai deposit and pyroxene wastes from the Koitash ore field wee developed. It was shown that by using nontraditional mineral raw material whose mineral composition is close to the compositions of standard fine ceramic pastes, ceramic materials with good thermomechanical and chemical properties can be obtained.

Production of construction materials for both special and decorative applications is one of the most dynamically developing sectors of industry in Uzbekistan. Clay, kaolin, different kinds of feldspar raw materials, quartz sand, and other types of materials are traditionally used in their production. Moreover, the current economic and geopolitical situation is such that research on introducing new kinds of nonmetallic mineral resources in ceramics practice to make articles with assigned properties and replace traditional materials with other, more economical materials is necessary.

The analysis of the published data and results of previous developments [1 – 5] showed that many nontraditional raw materials for a given region obtained from Republic deposits can be used in fabricating ceramic articles for different applications. This particularly concerns so-called porcelain stone from the Boinaksaiskoe deposit (Kashkadar'ya Oblast) and pyroxene wastes from the Koitashskoe deposit mining-concentration combine.

Porcelain stone is a specific group of hydrothermally altered rocks whose mineral and chemical compositions are close to the compositions of standard fine ceramic pastes, which allows considering them as a type of complex ceramic raw material.

Of the four previously identified geological-mineralogical types of stone, two are of the greatest interest — quartz-sericite and quartz-kaolinite-pyrophyllite varieties of porcelain stone. The ratio of rock-forming minerals is 55 – 60 and 30 – 35% in quartz-sericite rock. Quartz-kaolinite-pyrophyllite rock contains (%): up to 30% quartz, 50 – 60% pyrophyllite, and up to 30% kaolinite.

Pyroxene is a promising raw material. With respect to the mineral composition, pyroxene is basically represented by a solid solution based on diopside $Ca(Mg, Fe)SiO_6$ — a mineral that is almost insoluble in hydrochloric acid. Such high chemical resistance combined with relatively high mechanical strength allows pyroxene materials to successfully compete with the traditional acid-resistant materials used in the chemical industry.

In developing technology for manufacturing acid-resistant materials, acid-resistant tiles for construction in particular, we selected the optimum composition of pastes with the minimum necessary set of properties. In selecting the raw material, we departed from the basic premise that the batch for fabrication of ceramic materials usually contains three fundamental components: clay, leaning, and fluxes. We selected compositions that replaced existing kinds of raw material with little-studied materials while preserving their classic combination.

All raw materials were ground for 4 h to a particle size of less than 200 μm (dry grinding). Samples of different shape were prepared to study the properties of these materials. Preliminary tests on determining the degree of sintering were conducted on samples in the form of pellets 25 mm in diameter. The moisture content of the paste was 10%, and the molding pressure was 40 MPa. Standard samples were then prepared from pastes of the optimum composition by semidry molding to determine the compressive strength and heat resistance. The shrinkage and water absorption were monitored simultaneously. After the mechanical tests, the samples were additionally ground to a particle size of 0.8 – 1.0 mm and smaller and their acid resistance was measured according to GOST 473–81.

Several groups of compositions were developed parallelly. The ratio of the components was determined both by calculation and purely experimentally based on experience and published data [6 – 8]. In all groups, the clay component

[1] Institute of Materials Science, Physics – Sun Research and Production Association, Tashkent, Uzbekistan.

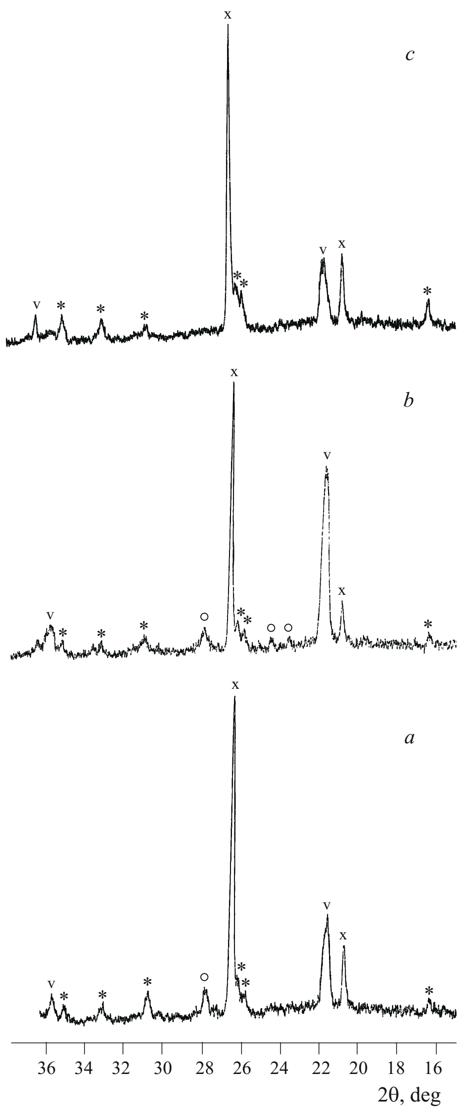

Fig. 1. Diffractograms of samples of UK-5 acid-resistant materials, firing temperature of 1250°C (*a*), KU-5, firing temperature of 1300°C (*b*), and UK-20, firing temperature of 1300°C (*c*): ∗) mullite; x) α-quartz; v) cristobalite; ○) anorthite.

was represented by Angrensk secondary unconcentrated kaolin. Refractory or acid-resistant chamotte or porcelain stone was used as the leaning material and pyroxene wastes were used as the flux. The leaning materials and fluxes were replaced by pegmatite and porcelain stone in the second group.

After analyzing the results obtained, several compositions (Table 1) with low water absorption and shrinkage were selected and samples were prepared from them for determining the thermomechanical properties. The results of these tests are reported in Table 2.

A comparison of the properties of the samples with chamotte or quartz-kaolinite-pyrophyllite rock (UK-178 and UK-20) as leaning agents showed that addition of porcelain stone together with pegmatite results in a better combination of shrinkage and water absorption — sintering is more complete with less shrinkage. This is due to the presence of pyrophyllite — a mineral that expands during firing and thus decreases the total shrinkage of the sample — in the porcelain stone.

TABLE 1

Composition	Mass content, %					
	Angrenskoe kaolin	chamotte	pegmatite	pyroxene wastes	quartz-kaolinite-pyrophyllite	quartz-sericite
UK-5	55	–	–	15	–	25
UK-16	55	–	–	10	–	35
UK-18	65	–	15	–	20	–
UK-20	75	15	10	–	–	–
KU-5	55	25	–	15	–	–

TABLE 2

Index*	Composition				
	UK-5	UK-16	UK-18	UK-20	KU-5
Firing temperature, °C	1250	1220	1300	1300	1300
Shrinkage, %	3.72	4.4	3.2	3.9	2.1
Water absorption, %	2.6	1.0	3.1	5.5	3.1
Acid resistance, %	91.3	92.5	98.1	99.7	99.9

* In all cases, the compressive strength was greater than 85 MPa and the heat resistance was greater than 8 thermal cycles (350 – 20°C).

The character of sintering differed strongly with an increase in the firing temperature in samples with the same amount of pyroxenes (compositions UK-16 and KU-5). In the samples with chamotte, the shrinkage increased insignificantly and the water absorption satisfied the requirements of the state standard. At the same time, the water absorption decreased to 1% but the shrinkage simultaneously increased sharply to 4.4% when the firing temperature was increased in the samples with quartz-sericite rock, which is undesirable for tiles.

In using pyroxene wastes as flux and selecting the leaning material, preference should thus be given to chamotte. The amount of pyroxenes in the paste should not exceed 15%,[2] since this mineral narrows the interval of the sintered state of the ceramic due to the sharp increase in the melt when the temperature is increased.

All samples had good mechanical strength and heat resistance, but differed in chemical resistance. Since they all had relatively close water absorption and strength values, it was obvious that the differences are due to their phase composition.

[2] Here and below: mass content.

The x-ray phase analysis of the samples showed the following. Silica in the form of α-quartz and cristobalite is the basic crystalline constituent. In addition, mullite is present in the amount of 10 – 15% while anorthite was present in the samples with pyroxene wastes (source of CaO) as one of the initial components (see Fig. 1). The presence of anorthite indicates that although the pyroxene wastes themselves have high chemical resistance, especially after melting and subsequent crystallization, when mixed with the other components, it actively reacts with them with formation of non-acid-resistant compounds.

As shown in [7], calcium oxide decreases the acid resistance of the articles, prevents synthesis of mullite, which has high chemical resistance, in the pastes, and causes formation of anorthite, whose solubility in boiling 50 – 70% sulfuric acid is 63 – 77%. For this reason, pastes containing anorthite should dissolve more actively in aggressive media. However, the simultaneous presence of a sufficient amount of mullite and/or cristobalite will neutralize the effect of the latter. In pastes containing the same amount of pyroxene wastes (15%), the acid resistance varied from 91.3 to 99.9% (compositions UK-5 and KU-5). The phase composition of these materials was primarily determined by the effect of the third (in addition to kaolin) component. When quartz-sericite rock was added, the amount of mullite and cristobalite in the paste decreased, and this decreased the chemical resistance.

In pastes containing no pyroxene wastes (samples UK-20 and UK-18), the acid resistance was determined to a significant degree by the amount of cristobalite, whose content varied as a function of the firing temperature and batch composition. When the pegmatite content in the batch increased due to an increase in the amount of clay in the chamotte or quartz-kaolinite-pyrophyllite rock, the amount of cristobalite decreased at the same firing temperature, and this reduced the acid resistance from 99.7 to 98.1%.

In production of acid-resistant materials, using pyroxene wastes as the flux and simultaneously incorporating either chamotte or quartz-kaolinite-pyrophyllite rock to the clay component are thus optimum. Without pyroxenes, it is preferable to use quartz-kaolinite-pyrophyllite rock, which contains minerals traditionally used in ceramic production. The results of these studies indicate that the use of nontraditional types of mineral raw material allows obtaining materials with good thermal, mechanical, and chemical properties.

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